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Article

Metal-free graphene quantum dots photosensitizer coupled with nickel phosphide cocatalyst for enhanced photocatalytic hydrogen production in water under visible light

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ABSTRACT

Photocatalytic hydrogen (H₂) evolution is a promising approach for future sustainable energy utilization. However, it is still a great challenge to develop efficient and stable metal-free photocatalysts with broadband solar absorption in the visible region for H₂ production. Metal-free graphene quantum dot (GQD) is an emerging candidate for this purpose because of its good water-solubility and tunable band gap. On the other hand, metal phosphides (Ni₂P, Co₂P, etc) have been demonstrated as novel noble-metal-free cocatalysts for water splitting, which can efficiently separate electron-hole pairs and enhance the photocatalytic activities. Herein, we report for the first time on the use of OH-functionalized GQDs (OH-GQDs) photosensitizer coupled with Ni₂P nanoparticles for photocatalytic H₂ production with $\lambda > 420$ nm light. The H₂ production rate is ~ 94 times higher than that of bare OH-GQDs, which is even comparable to that of OH-GQDs with 1.0 wt% Pt cocatalyst. This enhancement is probably due to the semiconductor-cocatalyst interface interaction between Ni₂P and OH-GQDs to facilitate efficient charge transfer process.

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1. Introduction

The development of clean and renewable energy resources has been one of the hot subjects in recent decades due to the global energy crisis and environmental issues [1,2]. Semiconductor mediated photocatalysis to produce H₂ is a promising method to solve this problem [3–6]. In the past decades, many efforts have been made to find suitable semiconductors for this purpose, such as TiO₂ [7–9], CdS [10–14], TaON [15,16]. Recently, metal-free nanocarbon-based photocatalysts have attracted increasing interest due to their following advantages: low cost, environmental friendly, and good stability [17–21].

Among them, graphene quantum dots (GQDs) have been suggested as a promising alternative to the conventional semiconductor quantum dots because of their unique properties such as high water-solubility, low toxicity, excellent biocompatibility, and high photostability [22–24]. Moreover, the band gaps of GQDs can be flexibly tuned by controlling the particle size and ligand species [25,26].

So far, bare metal-free GQDs have not been explored as a good photocatalyst for H₂ production under visible light, which is probably due to its short excitation lifetime, leading to fast electron-hole recombination, and thus poor photocatalytic efficiency [27,28]. The GQDs coupled with an efficient cocatalyst

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can probably solve this problem because of the existing fact of improved charge transfer from a semiconductor to a cocatalyst [29,30]. Traditionally, noble metals (such as Pt, Ru, and Pd) are regarded as the best cocatalysts for photocatalytic H_2 evolution when integrated with a semiconductor [31,32]. However, their high costs make it less attractive for practical application. In our previous studies [33–36], we found that metal phosphides could serve as good cocatalysts to enhance photocatalytic H_2 production. Among them, Ni_2P nanoparticles (NPs) were proved to be the most promising candidate as cocatalyst considering its good electrical conductivity and simple synthesis process [37,38].

Inspired by our previous studies, herein we report the use of water-soluble OH-functionalized graphene quantum dots (OH-GQDs) as the photosensitizer coupled with noble-metal-free Ni_2P NPs as the cocatalyst for visible-light driven H_2 production. Under optimal conditions, the highest photocatalytic H_2 evolution rate can reach $1567 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is ~ 94 times higher than that of bare OH-GQDs, suggesting that metal-free photosensitizer OH-GQDs coupled with noble-metal-free Ni_2P cocatalyst is efficient for photocatalytic H_2 evolution.

2. Experimental

2.1. Materials

All chemicals, including Pyrene ($C_{16}H_{10}$, 98.0%), Sodium hydroxide (NaOH, 96.0%), nitric acid (HNO_3 , 65~68%), ethylenediamine ($C_2H_4(NH_2)_2$, 99.0%), nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$, 98.0%), triethanolamine (TEOA, 99%), ascorbic acid (VC, 99.7%), methanol (CH_3OH , 99.5%), sodium sulfide nonahydrate ($Na_2S\cdot 9H_2O$, 99.0%), and anhydrous sodium sulfate (Na_2SO_4 , 97.0%), were commercially available (Aldrich and Innochem) and used without further purification.

2.2. Preparation of OH-GQDs

OH-GQDs were prepared according to a previous report with some modifications [39]. In a typical procedure, 2.0 g pyrene was nitrated into trinitropyrene in 160 mL hot HNO_3 at 80 °C under refluxing and stirring for 12 h. After cooling to room temperature, the trinitropyrene was collected by centrifugation. The resulting yellow precipitates were dispersed in 30 mL NaOH solution (0.2 mol/L) by ultrasonication for 150 min. The suspension was transferred to a Teflon-lined autoclave (50 mL) and heated for 10 h at 200 °C. After cooling to room temperature, the product containing water-soluble OH-GQDs was filtered through a 0.22 μm microporous membrane and then dialysed in a dialysis bag for 48 h. After that, the purified black OH-GQDs were dried at 80 °C under vacuum.

2.3. Preparation of Ni_2P NPs

Ni_2P NPs were synthesized according to our previous study [35]. Typically, a certain amount of $Ni(NO_3)_2\cdot 6H_2O$ and yellow phosphorus (1:5) were dissolved in ethylenediamine and

stirred for 30 min. Then, the mixed solution was transferred to a 50-mL Teflon-lined, stainless-steel autoclave and maintained at 140 °C for 12 h. After cooling to room temperature, the product was collected and washed with benzene, ethanol, and distilled water three times each.

2.4. Characterization

The crystal structures of the OH-GQDs and Ni_2P were characterized by powder X-ray diffraction (XRD, D/m/ax-TTR III) using graphite monochromatized Cu K_α radiation of 0.154178 nm, operating at 40 kV and 200 mA. The scanning range was from 10° to 70° (2θ) at the speed of 10° min^{-1} . Scanning electron microscopy (SEM) was performed on JSM-6700F. Transmission electron microscopy (TEM) images was collected on a JEM-2010 electron microscope, operated at an acceleration voltage of 200 kV. The chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 X-ray photoelectron spectrometer). Ultraviolet-visible (UV-vis) diffuse reflection spectra were investigated by using an UV-visible spectrophotometer (SOLID 3700 UV-vis spectrometer) over the range of 300 to 800 nm. The photoluminescence (PL) spectra were recorded on a FluoroMax-4 spectrometer at ambient temperature. Fourier transformed-Infrared spectroscopy (FTIR) spectra of dried samples were studied on a Thermo Fisher Scientific instrument (Nicolet iS10).

2.5. Photocatalytic hydrogen production

Photocatalytic H_2 evolution experiments were carried out in a 50 mL round-bottom flask at room temperature. A 300 W Xe-lamp equipped with a 420 nm cut-off filter was used to provide the visible light irradiation. In a typical run, 6 mg of the photocatalyst and 1.2 mg of the cocatalyst were dispersed in a mixed solution containing 18 mL water and 2 mL TEOA. Prior to irradiation, the solution was bubbled with high purity nitrogen for 15 min to remove the air inside. After that, 5 mL of methane was injected into the flask as the internal standard. The amount of produced H_2 was calculated by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) detector. For long-term irradiation, 20 mg of the photocatalyst and 4 mg of the cocatalyst were dispersed in a mixed solution containing 45 mL water and 5 mL TEOA and a 250 mL flask were used.

The apparent quantum yield (AQY) was measured using a 300 W Xe-lamp equipped with a 420 nm (± 5 nm) band-pass cut filter. The light intensity was approximately 6.8 mW cm^{-2} and the illuminated area for the reactor was approximately 27 cm^2 . The AQY was calculated based on the following equation (1):

$$\text{AQY} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \\ = \frac{\text{number of evolved } H_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

3. Results and discussion

The synthesis process of the OH-GQDs is shown in the Fig. 1 [39]. Typically, pyrene was nitrated in hot HNO_3 solution, followed by hydrothermal treatment in NaOH aqueous solution, and the as-prepared solution containing OH-GQDs was filtered. The filtrate was then dialysed in a dialysis bag for 48 h and dried at 80°C under vacuum. The OH-GQDs solution emits strong green fluorescence when irradiated under 365 nm UV light.

The structure of the OH-GQDs was characterized by XRD. The characteristic feature of graphite with a (002) layer spacing is clearly observed (Fig. 2(a)), which is consistent with that of bulk graphite (0.33 nm) [40]. Moreover, Fig. 2(b) shows the FTIR spectra of bare OH-GQDs. The peak at 1618 cm^{-1} can be assigned to the C=C bond stretch, and a strong, rather broad vibration at 3448 cm^{-1} is attributed to the O–H bonds [41]. Noticeably, a peak at 1271 cm^{-1} is also observed, corresponding to the vibration of C–OH [42,43]. All these results confirmed that the OH-GQDs were successfully synthesized. Furthermore, the surface chemical composition of the OH-GQDs was also studied by the EDX spectra. Fig. 2(c) shows the existence of C, O, and Cu elements. It should be noted that Cu element should be from the Cu grid substrate. In addition, the morphology and the particle size of the OH-GQDs were investigated by TEM. As shown in Fig. 2(d), the OH-GQDs particles are well dispersed with uniform lateral sizes at $3.6 \pm 0.5\text{ nm}$. In addition, the XRD pattern of the as-prepared Ni_2P cocatalyst shows good crystallinity (Fig. S1(a)). Fig. S1(b) is the SEM image of pure Ni_2P , in which small nanoparticles aggregated together with an average size of $\sim 300\text{ nm}$ were observed. The TEM image of $\text{Ni}_2\text{P}/\text{OH-GQDs}$ reveals that OH-GQDs are distributed randomly on Ni_2P (Fig. 3).

The light absorption of the OH-GQDs covers almost the entire visible light region, which make it very interesting for photocatalysis. The UV-vis absorption spectrum of the OH-GQDs sample is shown in Fig. 4(a). As can be seen, the absorption spectrum of the OH-GQDs have two pronounced peaks, max-

Fig. 3. TEM image of composite sample.

imized at about 350 and 490 nm, with an optical absorption edge extended to ~ 750 nm [44]. Its excellent absorbance in the visible region demonstrates great potential to generate H_2 under visible light [45]. Moreover, PL spectra of the OH-GQDs were measured under different excitation wavelengths. As shown in Fig. 4(b), when the excitation wavelength changes from 315 to 390 nm, the PL spectra have nearly the same features and show a strong emission peak at ~ 540 nm, suggesting a band gap of about 2.3 eV [46].

To identify the surface chemical compositions and valence states of the photocatalyst and cocatalyst, XPS was used to measure the OH-GQDs and Ni_2P samples. The high resolution C 1s XPS spectrum shows four peaks at the binding energy (BE) of 284.8, 285.7, 288.4, and 289.8 eV (Fig. 5(a)), which are ascribed to the strong signals of C=C, C–O, C–OH and C=O, respectively [39,47,48]. Meanwhile, the high-resolution O 1s XPS spectrum reveals the presence of O–H at 531.6 and 533.1 eV (Fig. 5(b)). The peak at 531.6 eV belongs to OH-GQDs [39] and the signal at 533.1 eV is assigned to the absorbed water [49,50]. The XPS results further confirmed the successful synthesis of OH-functionalized GQDs. Moreover, the XPS spectrum of Ni 2p (Fig. 5(c)) shows two main typical peaks (857.1 and 874.8 eV) with satellite peaks (marked as “Sat.”) and a very weak peak at 853.3 eV is attributed to Ni^{2+} of Ni_2P [51]. The peaks at the BE of 857.1 and 874.8 eV, along with their satellite peaks, corre-

spond to the Ni^{2+} originating from surface oxidation state. Fig. 5(d) gives the high resolution P 2p XPS spectrum. The peaks at the BE of 129.3 and 130.2 eV can be ascribed to the reduced phosphorus in the form of metal phosphides, while the peak at 134.1 eV can be assigned to oxidized P species due to air exposure [52]. The XPS results further proved the formation of Ni_2P with surface partially oxidized to phosphate.

Based on the above characterizations and analysis, the photocatalytic H_2 production experiments of the present OH-GQDs coupled with Ni_2P cocatalyst ($Ni_2P/OH-GQDs$) were further evaluated in aqueous solution under visible light ($\lambda > 420$ nm) [53]. Firstly, the effect of different sacrificial agents was investigated (0.75 mol/L ascorbic acid, pH = 4.2; 0.75 mol/L methanol; 0.75 mol/L TEOA; 0.31 mol/L Na_2S /0.44 mol/L Na_2SO_3). The results show that only the TEOA solution can produce apparent H_2 , indicating that the weak alkaline condition might be favorable for photocatalytic H_2 production using $Ni_2P/OH-GQDs$ (Fig. 6(a)). In order to explore the reason why only the TEOA solution can produce apparent H_2 , the PL spectra were measured. The concentrations of OH-GQDs for four different sacrificial agents are the same. As shown in Fig. S2(a), the emission intensity of $Ni_2P/OH-GQDs$ (black line) was significantly quenched when TEOA was added (red line), indicating that the electron-hole recombination can be efficiently suppressed in the presence of TEOA. However, for methanol and Na_2S/Na_2SO_3 , the PL intensities only slightly decreased (Fig. S2(b) and (c)). Interestingly, in the presence of VC (Figure S2d), the PL spectrum has been interrupted and damaged, which is probably caused by the VC solution. Based on the PL results, we can conclude that TEOA is the most efficient electron donor, which can quickly capture photo-generated holes and thus promoting the H_2 evolution reaction.

Fig. 6(b) displays the rate of H_2 production using bare OH-GQDs, bare Ni_2P , $Ni_2P/OH-GQDs$, and 1 wt% Pt/OH-GQDs samples in 0.75 mol/L TEOA solution [54]. As can be seen, Ni_2P itself is not active for H_2 evolution under visible light. Moreover, as for bare OH-GQDs, trace H_2 production was detected, although it has a strong absorption band in visible region. The poor activity of pure OH-GQDs could be ascribed to the fast recombination of photo-generated electron-hole pairs [55]. Interestingly, it was found that an appropriate amount of Ni_2P

Fig. 4. (a) UV-Vis absorption spectrum of OH-GQDs dispersed in 3 mL water, the inset picture is the photograph of aqueous colloids of OH-GQDs under 365 nm light. (b) Photoluminescence spectra of OH-GQDs at different excitation wavelengths.

Fig. 5. High-resolution XPS spectra of C 1s (a), O 1s (b), Ni 2p (c), and P 2p (d).

can significantly enhance the photocatalytic activity for H_2 production using $\text{Ni}_2\text{P}/\text{OH-GQDs}$ sample. Noticeably, the rate of H_2 evolution initially increased with the increasing amounts of Ni_2P and then decreased with more amount of Ni_2P . The highest photocatalytic H_2 evolution rate of $\sim 1567 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ was obtained when 20 wt% Ni_2P was used, which is comparable to the activity of 1 wt% $\text{Pt}/\text{OH-GQDs}$ ($\sim 1683 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). When the weight ratio of Ni_2P reached more than 20 wt%, the H_2 evolution rate decreased ($\sim 1000 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ for 30 wt%), probably resulting from the fact that more Ni_2P per unit area can shield the visible light absorption of OH-GQDs , leading to the decrease of photons absorbed. Interestingly, the present photocatalytic reaction system also showed good photocatalytic activity when the reaction solution was exposed to air (Fig. 6(c)). All the above results suggest the importance of noble-metal-free Ni_2P cocatalyst for the improvement of H_2 evolution over OH-GQDs . To the best of our knowledge, this is the first time to explore the photocatalytic activity of OH-GQDs for H_2 production coupled with a noble-metal-free cocatalyst.

The apparent quantum yield (AQY) for H_2 evolution over the 20 wt% $\text{Ni}_2\text{P}/\text{OH-GQDs}$ photocatalyst was performed in a system containing 0.75 mol/L TEOA under a monochromatic light at 420 nm (± 5 nm). As shown in Fig. 6(d), the AQY increases with the irradiation time, especially in the initial stage, which may be due to an induction period and the dissolved H_2 in the solution [35]. H_2 was not detected until the sample was irradiated for 2 h. The AQY is only 0.2% for the second hour and then reaches to 0.64% with a H_2 evolution rate up to $\sim 428.5 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ after 8 h of irradiation. The average AQY is 0.46%

in the evaluated time. Meanwhile, the stability of the $\text{Ni}_2\text{P}/\text{OH-GQDs}$ under a 300 W Xe lamp with a 420 nm (± 5 nm) band-pass filter was also studied (Fig. 7(a)). No significant decrease for photocatalytic H_2 production was observed. After 28 h of irradiation, a total amount of $\sim 199.8 \mu\text{mol}$ H_2 was produced at a constant rate of $\sim 440 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, suggesting excellent durability of the $\text{Ni}_2\text{P}/\text{OH-GQDs}$ for photocatalytic H_2 production under visible light.

In order to explore the reaction mechanism for photocatalytic H_2 production over $\text{Ni}_2\text{P}/\text{OH-GQDs}$, the Mott-Schottky plot and PL measurements were examined to study the photoinduced electron transfer behavior. Fig. 7(b) shows the Mott-Schottky plot of OH-GQDs in a H_2SO_4 solution (1.0 mol/L) and the positive slope indicates n-type conductivity [56]. Moreover, the Fermi levels (E_{Fn}) of the OH-GQDs could be gained from the X-intercept by extrapolating the M-S plot to $1/C^2 = 0$, and the values for the sample is about -0.52 V vs. NHE, which is consistent with previous reports [27,28]. Therefore, the conduction band of the OH-GQDs is more negative than -0.52 V vs. NHE (E_{Fn}). In the previous studies, the photo-excited carriers can be swiftly transferred from the CB of CdS (-0.5 V vs. the NHE) to Ni_2P , which acts as an excellent cocatalyst [57,58]. Since the CB edge of OH-GQDs is more negative than that of CdS , the photo-excited electrons on OH-GQDs could be transferred to Ni_2P through the $\text{Ni}_2\text{P}/\text{OH-GQDs}$ interface. The emission intensity was obviously quenched upon adding Ni_2P to the OH-GQDs solution (Fig. 7(c)), indicating Ni_2P can suppress the electron-hole recombination [59,60]. According to the aforementioned results, a probable reaction mechanism for the

Fig. 6. (a) Hydrogen production rate on 20 wt% Ni₂P/OH-GQDs photocatalyst with different types of the hole scavenger (TEOA, VC, methanol, and Na₂S/Na₂SO₃) at room temperature under visible light ($\lambda > 420$ nm). (b) The rate of H₂ evolution over Ni₂P/OH-GQDs photocatalyst hybrid with different amounts of Ni₂P at room temperature under visible light ($\lambda > 420$ nm), and comparison of photocatalytic H₂ evolution with 1 wt% Pt. The system contains 6 mg photocatalyst, 1.2 mg cocatalyst and 2 mL TEOA in 18 mL deionized water. (c) Comparison of photocatalytic H₂ evolution under N₂ and in air. Both systems contain the same components: 18 mL H₂O and 2 mL TEOA in the presence of 6 mg photocatalyst and 1.2 mg cocatalyst. (d) The time courses of H₂ evolution and the average apparent quantum yield (AQY) over the 20 wt% Ni₂P/OH-GQDs photocatalyst under monochromatic 420 nm light irradiation. The bars denote the apparent quantum yield.

Fig. 7. (a) Long-term production of H₂ for 28 h under monochromatic 420 nm light irradiation using 20 wt% Ni₂P/OH-GQDs photocatalyst at room temperature. (b) Mott-Schottky curve of OH-GQDs in 1.0 mol/L H₂SO₄. (c) Spectra performance of the pure OH-GQDs and 20 wt% Ni₂P/OH-GQDs photocatalyst at an excitation wavelength of 315 nm at room temperature.

enhanced photocatalytic activity of the Ni₂P/OH-GQDs is proposed. As shown in Scheme 1, OH-GQDs ($E_g = 2.3$ eV) can effectively absorb visible light to excite electrons located at the valence band (VB) to the conduction band (CB), accompanied by the creation of photogenerated electron-hole pairs [61]. In addition, Ni₂P shows metallic character and can not absorb visible light to produce electron-hole pairs [62]. Due to the introduction of Ni₂P on OH-GQDs, a typical metal-semiconductor interface was formed. Then, the photo-generated electrons in the CB of OH-GQDs rapidly moved to the surface of the Ni₂P NPs and

the holes could be consumed by TEOA, and thus promoting separation of the electron-hole pairs and suppressing their recombination. Finally, the electrons on the surface of Ni₂P will catalyze the reduction of protons to produce H₂, resulting in the improved photocatalytic H₂ production activity.

4. Conclusions

In summary, we studied the use of OH-GQDs as a metal-free photosensitizer for photocatalytic H₂ evolution under visible

Scheme 1. Schematic illustration of the mechanisms for the photocatalytic H_2 evolution over $\text{Ni}_2\text{P}/\text{OH-GQDs}$ under visible light irradiation.

light. The photocatalytic activity can be significantly enhanced by the addition of noble-metal-free Ni_2P cocatalyst. Under optimal conditions, the photocatalyst sample exhibited a maximum H_2 evolution rate of $1567 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is ~ 94 times higher than that of bare OH-GQDs and comparable to the catalytic activity of 1 wt% Pt/OH-GQDs sample ($1683 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). All the results indicate that Ni_2P can efficiently promote the separation of photo-generated charge carriers and highly enhance photocatalytic H_2 evolution of OH-GQDs. This present study demonstrates that the OH-GQDs is an efficient metal-free catalyst for photocatalytic H_2 evolution coupled with a suitable cocatalyst.

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Graphical Abstract

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Metal-free graphene quantum dots photosensitizer coupled with nickel phosphide cocatalyst for enhanced photocatalytic hydrogen production in water under visible light

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Metal-free OH-functionalized graphene quantum dots (OH-GQDs) were used as the photosensitizer coupled with Ni₂P nanoparticles (NPs) for photocatalytic H₂ production under visible light. The H₂ production rate is ~94 times higher than that of bare OH-GQDs, which is even comparable to that of OH-GQDs with 1 wt% Pt cocatalyst. This enhancement is probably due to the semiconductor-cocatalyst interface interaction between Ni₂P and OH-GQDs to facilitate efficient charge transfer process.

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非金属光敏剂石墨烯量子点与磷化镍耦合用于可见光光催化制氢

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摘要: 利用光催化反应制取氢气是满足未来能源可持续利用的一个很有效的方法。然而, 如何去开发和利用高效且稳定的非金属光催化剂用于产氢反应是目前所面临的一个巨大的挑战。最近, 非金属纳米碳基材料由于其诸多优点而吸引了人们广泛的关注, 比如价格低廉、环境友好和良好的稳定性等。另外, 石墨烯量子点由于具有很好的水溶性、低毒性, 良好的生物兼容性和很好的光学稳定性等优点而被当作是一种能够替代传统量子点的很有前途的材料。除此之外, 石墨烯量子点的带隙还可以通过控制其颗粒大小和其表面所带的官能团来进行灵活调控。另一方面, 金属磷化物(磷化镍、磷化钴等)已经被证实了是很好的水分解制氢的非贵金属助催化剂, 它们可以加快光生电子和空穴的分离, 从而提高光催化活性。

本文利用非金属光敏剂石墨烯量子点与非贵金属助催化磷化镍进行耦合制备复合光催化剂, 实现了在可见光照射下进行光催化制氢。在最优条件下, 复合光催化剂的产氢速率为空白石墨烯量子点的94倍, 甚至与在空白量子点上负载1.0 wt% Pt的产氢速率相当。产氢速率的大幅度提升可能是由于在石墨烯的量子点和磷化镍之间形成了半导体-金属接触界面, 从而更有效地促进了光生载流子的传输过程。

石墨烯量子点本身有着很好的水溶性, 从而利用机械搅拌的方法与磷化镍进行耦合, 并在可见光下进行产氢反应。本

文采用红外光谱(FTIR)、透射电镜(TEM)、紫外可见光谱(UV-Vis)和荧光光谱(PL)等表征手段研究了空白量子点表面所带的官能团、尺寸大小和光学性能。采用TEM和PL等表征手段来研究复合光催化剂的形貌和产氢性能提高的原因。

对于空白量子点, FTIR结果表明, 其表面带有–OH等官能团; TEM结果表明, 它的尺寸大小大概在 3.6 ± 0.5 nm; UV-Vis结果表明, 其在可见光区域有着很强的光吸收; PL结果表明, 其在波长约为540 nm处有着很强的吸收峰, 所对应的带隙约为2.3 eV。对于复合光催化剂, TEM测试结果表明石墨烯量子点在磷化镍上随机分布; 从PL结果可见, 复合光催化剂的荧光强度明显降低, 说明了光生电子从量子点到磷化镍的有效转移, 这也是光催化活性提高的重要原因。

关键词: 非贵金属; 光催化; 产氢; 石墨烯量子点; 磷化镍

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